

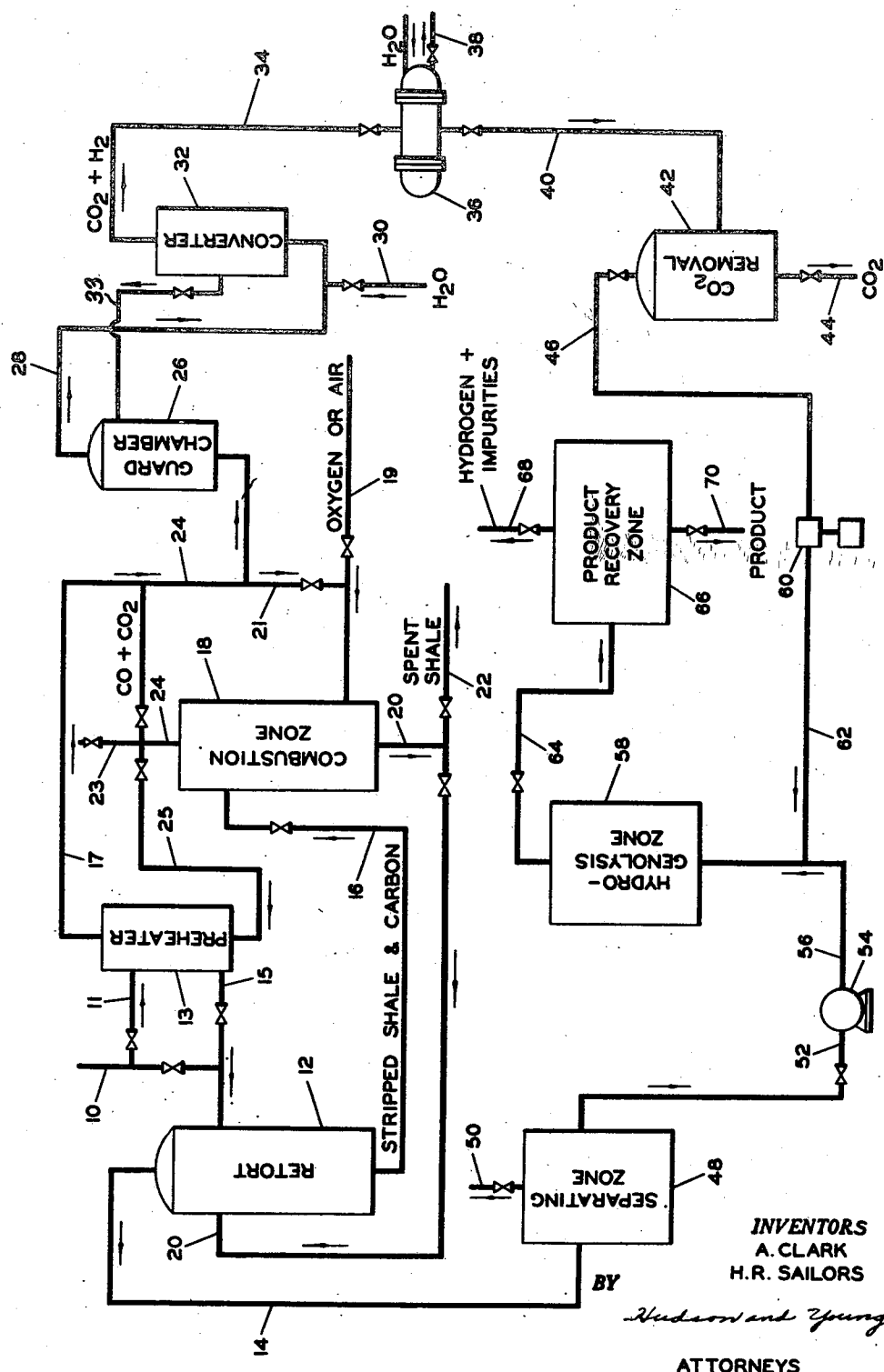
June 28, 1949.

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2,474,345

RECOVERY OF HYDROCARBONS FROM OIL SHALE

Filed May 19, 1947



## UNITED STATES PATENT OFFICE

2,474,345

## RECOVERY OF HYDROCARBONS FROM OIL SHALE

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Application May 19, 1947, Serial No. 749,063

3 Claims. (Cl. 196—53)

1

This invention relates to the production of organic material from oil shale and the like. One embodiment of this invention relates to the retorting step for distilling organic matter from oil shale. In one specific embodiment this invention relates to volatilizing organic material from oil shale and treating a portion of said organic material with hydrogen manufactured in the process.

The existence of oil in oil shale has been known for many years, and relatively small scale operations for the recovery of this oil have been carried out in this country. In foreign countries where petroleum is not plentiful the recovery and utilization of this oil have been carried out more extensively.

The usual method for the recovery of this oil is by distillation of the oil from the shale in a retort with recovery of the vaporized material, for example, by condensation. The distillation leaves a residue of shale covered and/or impregnated with a carbonaceous deposit. The residue, with its carbonaceous deposit, may then be charged to a combustion zone to accomplish the heating of the retort by direct firing.

The organic product recovered by this procedure is a very unstable product and readily oxidizes to form gum and other deleterious products. The recovered product, therefore, must be stabilized prior to use in most cases and particularly prior to use as motor fuels. With an efficient condensing system, the recovered product usually contains hydrocarbons boiling over a wide range, including normally gaseous hydrocarbons through those boiling in the range of gas oil, as well as appreciable amounts of oxygen-, sulfur-, and nitrogen-containing organic compounds.

According to the present invention, the retorting of oil shale is carried out in an advantageous manner by combining in a distillation zone fresh oil shale with hot shale from a combustion zone, the hot shale furnishing at least a major portion of the heat necessary for the distillation of the hydrocarbons in the fresh shale, and the stripped shale from the distillation zone, carrying with it a carbonaceous deposit, is conducted to a combustion zone. In the combustion zone, the carbonaceous deposit is burned with oxygen or suitable oxygen-containing gas and a portion of the hot shale is returned to the distillation zone to furnish heat for the retorting or distillation of additional fresh oil shale. In a further modification of this invention, the carbon monoxide from the combustion zone may be utilized in the manufacture of hydrogen, which

2

may in turn be used to refine by hydrogenolysis organic products of the distillation zone.

An object of this invention is to recover organic material from oil shale.

Another object of this invention is to recover hydrocarbons from oil shale.

Another object is to recover oil from oil shale and to convert said oil to a stable product.

Still another object is to provide a process for recovering oil from oil shale by distillation, manufacturing hydrogen in a step in said process and hydrogenating at least a portion of the product obtained from the distillation step.

Still other objects and advantages of the present invention will become apparent to those skilled in the art from the accompanying disclosure and description.

One embodiment of this invention is shown diagrammatically by the accompanying drawing. In the description of this drawing the various process steps will be described in connection with appropriate conditions for their operation, which will serve as examples thereof.

Oil shale, from a source not shown, is conducted by suitable means through line 10 to retort 12. Hot shale from combustion zone 18 is added to said retort through line 20. The hot shale heats the fresh oil-containing shale and organic material is distilled from this fresh shale. A carbonaceous deposit remains on the shale. The organic products of this distillation are removed from the retort through line 14 to further processing to be described. The stripped shale is removed from retort 12 through line 16 to combustion zone 18. Though not shown, a portion of this stream may be discarded and only the portion needed to furnish heat by the combustion step and recycle to be described may be charged to the combustion zone 18.

Oxygen or suitable oxygen-containing gas, such as air, is charged to combustion zone 18 through line 19. Where no use is to be made of the carbon oxides formed in this step, air is the better gas to be charged to the combustion zone, though in such cases where it is desirable to use the carbon monoxide formed to manufacture hydrogen, it may be more desirable to use relatively pure oxygen in order to avoid dilution of the hydrogen produced with the nitrogen from air. Dilution of the oxygen or air charged to the combustion zone may be accomplished by recycling cooled flue gases, these recycle gases from a source to be described being conducted through line 21 to line 19, there joining the oxygen or air stream prior to entry into the com-

bustion zone. In the combustion zone the carbon on the shale is burned and the shale heated by this combustion. The hot shale is removed from combustion zone 18 through line 20 and a portion may be discarded through line 22. The retained portion of the hot shale is conducted through the remaining length of line 20 to retort 12, thence following a previously described route.

In the system just described the recycle of the shale to the distillation or retorting zone provides the heat to carry out the distillation step. Thus the temperature of the retort may be controlled by controlling the amount and the temperature of the hot shale charged to retort 12. The amount of hot shale recycled—and thus the ratio of fresh oil shale to hot recycle shale—is controlled by the proportion of the hot shale discarded through line 22. The temperature of the shale from the combustion zone may in turn be controlled by the recycle of the cooled combustion gas. The system thus provides for temperature control in both zones without a great amount of interdependence between the two zones.

If desired, fresh oil shale flowing through line 10 may be passed through preheater 13 by way of lines 11 and 15 where the oil shale is preheated by means of heat exchange with the hot combustion gases from combustion zone 18 prior to the oil shale entering retort 12. For this auxiliary preheating system hot combustion gases are withdrawn from line 24 and passed through line 25 to preheater 13 and back through line 17 through line 24.

The temperature in retort 12 may vary between about 400 to 1,200° F. but preferably the temperature is maintained in a range of about 700 to 1,000° F. The exact temperature employed depends to some extent upon the particular oil shale undergoing treatment and other factors such as size of the oil shale particles, residence time in the retort and the like. The size of the oil shale particles charged to retort 12 may vary from a powder to about one-half inch in diameter; however, particle sizes coming in the range of about 4 to 100 mesh are preferable. The ratio of the fresh oil shale to the spent shale from the combustion zone may vary over a considerable range, also depending on the temperature desired in the retort and the temperature of the shale from combustion zone; however ratios of fresh oil shale to shale from combustion zone may range from about 5:1 to 1:10 but a ratio of about 2:1 to 1:2 is preferred. The residence time of the oil shale in retort 12 may vary from about 1 minute to about 15 minutes but about 3 to 8 minutes is preferable. Temperature of the combustion zone may approach the sintering temperature of the shale, which will vary with the particular shale undergoing treatment, but is usually maintained below about 2,500° F. and preferably between about 1,500 and about 1,900° F. The oxygen-containing gas and the stripped shale containing carbonaceous material are brought together by countercurrent flow in the combustion zone in suitable proportions to maintain the temperature in the combustion zone within the desired range and at the same time produce a high ratio of carbon monoxide to carbon dioxide. The amount of oxygen should be so regulated that there is little or no free oxygen in the effluent combustion gases. It is preferable to operate retort and combustion zone at about atmospheric pressure, though superatmospheric pressure may be used.

The hot combustion gases in combustion zone

18 are removed through line 24. If desired, a portion or all of these may be discarded through line 23. In this particular embodiment, however, it is desired to produce hydrogen by a process in which the carbon monoxide produced in this step is used. It is therefore desirable to charge oxygen to the combustion zone through line 19 and remove hot combustion gases from the zone having a low inert gas content. The gases removed through line 24 are cooled by a heat exchanger, not shown, or by passing therein through preheater 13 as outlined above and a portion recycled as oxygen diluent through line 21, as previously described. The remaining portion of this stream is conducted through said line 24 to guard chamber 26, containing spent catalyst from a source to be described, where sulfur compounds and/or other deleterious compounds are removed or converted to relatively innocuous forms. Other methods, however, may be used in place of or in conjunction with this method to remove these undesirable compounds if desired. The purified gas is removed from guard chamber 26 through line 28, additional water or steam then added through line 30, and the total stream conducted through said line 28 to converter 32. This converter is filled with a suitable catalyst, such as an iron catalyst, to catalyze the reaction of carbon monoxide and steam to form hydrogen and carbon dioxide. This reaction is favored by excess steam, being an equilibrium reaction. With an iron catalyst, suitable temperatures are from about 800 to about 1,000° F. With other catalysts, the converter should be operated at temperatures suitable to the particular catalyst employed. The spent catalyst from this chamber may be charged to guard chamber 26, thus obtaining further useful life from this material in removing compounds deleterious to active catalyst. The gas stream removed from converter 32 is predominantly steam, carbon dioxide, and hydrogen. This stream is removed through line 34 and conducted to cooling zone 36, where the steam is condensed and removed as water through line 38. Carbon dioxide and hydrogen are removed through line 40 to carbon dioxide removal zone 42. The removal of the carbon dioxide may be accomplished by any of the many suitable methods disclosed in the art, such as the tri-ethanol-amine method. Carbon dioxide is removed from zone 42 through line 44 and conducted to suitable disposition, not shown. The remaining gases, predominantly hydrogen, are removed through line 46.

The organic material distilled from the shale in retort 12 is conducted through line 14 to separating zone 48 which may consist of conventional equipment for separating the light components such as butane and lighter. These light gases are removed through line 50 to suitable utilization, not shown. Pentane and heavier components of the stream are removed from separation zone 48 through line 52 and passed to pump 54, and then conducted to hydrogenolysis zone 58 through line 56.

Line 46 conducts the hydrogen stream to compressor 60, then via line 62 this stream is conducted to line 56, where it joins the hydrocarbon stream carried by that line and thence is conducted to the hydrogenolysis zone 58.

In the hydrogenolysis zone, the stream of organic material and hydrogen is heated to a suitable temperature, from 800 to 1,000° F. and preferably from 850 to 950° F., and contacted with a catalyst, preferably molybdenum trioxide, al-

though other known hydrogenation catalysts may be used if desired. The hydrogenolysis may be carried out at pressures from 1,000 to 10,000 pounds per square inch, though preferably from 2,000 to 5,000 pounds per square inch. The treated product from this zone is removed through line 64 to product recovery zone 66 where hydrogen and by-product impurities are separated from the product and removed through line 68. The treated product is withdrawn from zone 66 through line 70.

In the hydrogenolysis zone, the organic material treated is improved by a substantial reduction of the sulfur, oxygen and/or nitrogen content of the organic material. These elements appear in the effluent as nitrogen or ammonia, water and/or hydrogen sulfide which may readily be removed by conventional treatment, and the major portion of the non-hydrocarbon organic material is converted to hydrocarbons.

Though not shown in the drawing, the feed to the hydrogenolysis zone may be treated in fractions of various boiling ranges, and most suitable conditions of treatment chosen for each fraction. Such treated fractions may be reblended with each other and with other products, if desired, in any predetermined proportion to meet certain product specifications, for example, motor fuel.

#### Example

In a process similar to that illustrated in the drawing, 500 pounds of a non-bituminous oil-bearing shale containing about 10 weight per cent recoverable organic material is charged into the top of a retort simultaneously with 500 pounds of hot spent shale having a temperature of about 1,800° F. so that the temperature in the retort is maintained at about 900° F. Fifty pounds of organic material is recovered from the oil shale. This organic material has the following properties:

Gravity, °API—about 40.

Color—dark.

Boiling range—initial boiling point, 120° F.; 50% over at 570° F.

The stripped shale containing carbonaceous material is removed from the retort and is passed to a furnace where the carbonaceous material is burned off in the presence of oxygen. The stripped shale sent to the furnace contains about 1-2 weight per cent carbonaceous material. The burning of stripped shale is controlled so that the effluent flue gas contains 60-70 volume per cent of carbon monoxide. The temperature in the furnace is held at about 1,800° F.

The recovered hydrocarbon is subjected to hydrogenolysis over molybdenum oxide (9 weight per cent) on alumina at a temperature of 900° F., 5,000 p. s. i. and a space velocity of about 1 liquid volume per hour per volume of catalyst. The C<sub>2</sub> hydrocarbon effluent consists of about 50 volume per cent gasoline. The heavy fraction boils below 700° F., and is suitable for use as Diesel fuel.

In the drawing, numerous pumps, conveyors, and other miscellaneous equipment are not shown, but these may readily be supplied by one skilled in the art. Other modifications and variations of this invention may obviously be used and can be adapted by one skilled in the art without departing from the spirit of the disclosure, and without departing from the scope of the claims.

We claim:

1. A process for the recovery of a hydrocarbon

material from oil-bearing shale, which comprises admixing in a retorting zone hot spent shale from a combustion zone and particles of oil-bearing shale, which particles are not greater than 0.5 inch in diameter, maintaining the ratio of said hot spent shale to said oil-bearing shale such that the temperature in said retorting zone is maintained in the range of 700 to 1000° F. and dislodging organic material from said oil-bearing shale, separating said resulting organic material from said retorting zone; withdrawing stripped shale containing residual carbonaceous material from said retorting zone and introducing at least a portion of said stripped shale into a combustion zone, introducing oxygen into said combustion zone, maintaining a temperature in said combustion zone in the range of 1500 to 1900° F. and converting said residual carbonaceous material retained by said stripped shale to carbon monoxide; withdrawing the resulting hot spent shale from said combustion zone and recycling at least a portion of said hot spent shale to said retorting zone; withdrawing carbon monoxide-containing material from said combustion zone and recycling a portion of said carbon monoxide-containing material to said combustion zone in admixture with said oxygen; preheating at least a portion of said oil-bearing shale with another portion of said carbon monoxide-containing material prior to introduction of said oil-bearing shale into said retorting zone; treating at least a portion of said carbon monoxide-containing material to remove impurities, and subsequently admixing resulting carbon monoxide with steam and passing the resulting mixture over an iron catalyst maintained at a temperature in the range of 800 to 1000° F. and converting carbon monoxide and steam to hydrogen and carbon dioxide; treating at least a portion of the resulting mixture, comprising hydrogen and carbon dioxide, to remove the carbon dioxide; simultaneously passing at least a portion of said organic material and purified hydrogen over a molybdenum trioxide catalyst maintained at a temperature in the range of 850 to 950° F. and at a pressure of from 2,000 to 5,000 pounds per square inch and hydrogenating said organic material and recovering a resulting hydrocarbon material as a product of the process.

2. A process for the recovery of a hydrocarbon material from oil-bearing shale, which comprises admixing in a retorting zone hot spent shale from a combustion zone and particles of oil-bearing shale, which particles are not greater than 0.5 inch in diameter, maintaining the ratio of said hot spent shale to said oil-bearing shale such that the temperature in said retorting zone is maintained in the range of 400 to 1200° F. and dislodging organic material from said oil-bearing shale, separating said resulting organic material from said retorting zone; withdrawing stripped shale containing residual carbonaceous material from said retorting zone and introducing at least a portion of said stripped shale into a combustion zone, introducing oxygen into said combustion zone, maintaining a temperature in said combustion zone in the range of 1500 to 2500° F. and converting said residual carbonaceous material retained by said stripped shale to carbon monoxide; withdrawing the resulting hot spent shale from said combustion zone and recycling at least a portion of said hot spent shale to said retorting zone; withdrawing carbon monoxide-containing material from said combustion zone and recycling at least a portion of said carbon monoxide-containing material to said combustion zone in admix-

ture with said oxygen; preheating at least a portion of said fresh oil-bearing shale with another portion of said carbon monoxide-containing material prior to introduction of said oil-bearing shale into said retorting zone; treating at least a portion of said carbon monoxide-containing material to remove impurities, and subsequently admixing resulting carbon monoxide with steam and passing the resulting mixture over an iron catalyst maintained at a temperature in the range of 800 to 1000° F. and converting the carbon monoxide and steam to hydrogen and carbon dioxide; treating at least a portion of the resulting mixture, comprising hydrogen and carbon dioxide, to remove the carbon dioxide; simultaneously passing at least a portion of said organic material and purified hydrogen over a molybdenum trioxide catalyst maintained at a temperature in the range of 800 to 1000° F. and at a pressure of from 1,000 to 10,000 pounds per square inch and hydrogenating said organic material and recovering a resulting hydrocarbon material as a product of the process.

3. A process for the recovery of a hydrocarbon material from oil-bearing shale, which comprises admixing in a retorting zone hot spent shale from a combustion zone and particles of oil-bearing shale, maintaining the ratio of said hot spent shale to said oil-bearing shale such that a suitable temperature is maintained in said retorting zone to dislodge organic material from said oil-bearing shale, separating said resulting organic material from said retorting zone; withdrawing stripped shale containing residual carbonaceous material from said retorting zone and introducing at least a portion of said stripped shale into a combustion zone, introducing oxygen into said combustion zone, maintaining a suitable temperature in said combustion zone to convert said

residual carbonaceous material retained by said stripped shale to carbon monoxide; withdrawing the resulting hot spent shale from said combustion zone and recycling at least a portion of said hot spent shale to said retorting zone; withdrawing carbon monoxide-containing material from said combustion zone and treating at least a portion of said carbon monoxide-containing material to remove impurities, and subsequently admixing resulting carbon monoxide with steam and passing the resulting mixture over a suitable catalyst in a conversion zone under such conditions that the carbon monoxide and steam are converted to hydrogen and carbon dioxide; treating at least a portion of the resulting mixture, comprising hydrogen and carbon dioxide, to remove the carbon dioxide; treating at least a portion of said organic material with purified hydrogen in the presence of a suitable hydrogenation catalyst maintained under such conditions that said organic material is hydrogenated and recovering a resulting hydrocarbon material as a product of the process.

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